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## RESEARCH LETTER

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## Key Points:

- The roles of organic acids, amines, inorganic acids, and highly oxidized organics are analyzed for two new particle formation events using in situ observations
- Saturated linear organic acids are the particulate species most associated with the appearance of new 20–50 nm particles
- The event days were associated with rapid transport of marine air to the site

## Supporting Information:

- Supporting Information S1

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## Evidence for Diverse Biogeochemical Drivers of Boreal Forest New Particle Formation

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**Abstract** New particle formation (NPF) is an important contributor to particle number in many locations, but the chemical drivers for this process are not well understood. Daytime NPF events occur regularly in the springtime Finnish boreal forest and strongly impact aerosol abundance. In April 2014 size-resolved chemical measurements of ambient nanoparticles were made using the Time-of-Flight Thermal Desorption Chemical ionization Mass Spectrometer and we report results from two NPF events. While growth overall was dominated by terpene oxidation products, newly formed 20–70 nm particles showed enhancement in apparent alkanolic acids. The events occurred on days with rapid transport of marine air, which correlated with low background aerosol loading and higher gas phase methanesulfonic acid levels. These results are broadly consistent with previous studies on Nordic NPF but indicate that further attention should be given to the sources and role of non-terpenoid organics and the possible contribution of transported marine compounds in this process.

**Plain Language Summary** Clouds are an enormously important part of the climate system because they control the radiation entering and leaving the Earth. Clouds form as water condenses onto small particles called cloud condensation nuclei. These particles can be directly emitted from the Earth's surface, like sea spray, for example, or they can form in the atmosphere out of precursor gases. We have measured the composition of these atmosphere-formed particles to understand better how this process works in the Nordic boreal forest. We found that a diverse mix of processes and molecules are likely involved, possibly including the transport of materials from the ocean. While these results will ultimately lead to a better understanding of ocean-land-cloud interactions, they currently indicate that more work is needed to learn the processes involved.

## 1. Introduction

Atmospheric particles are important for the climate system due to their direct interaction with radiation and their role in cloud formation. The majority of atmospheric particles are generated by new particle formation (NPF) (Merikanto et al., 2009; Spracklen et al., 2006) which proceeds by homogeneous nucleation and subsequent growth due to net uptake of gas phase species (Kuang et al., 2010; Kulmala et al., 2004; McMurry, 1983; Zhang et al., 2012). However, the relative impact of NPF on global radiative forcing compared with directly emitted particles is less clear. This is due to uncertainties about the chemical mechanisms of nucleation and the efficiency with which newly formed particles are able to grow to sizes at which they can directly interact with shortwave radiation and/or act as cloud condensation nuclei (e.g., Spracklen et al., 2008).

New particle formation has been a topic of intense study at the Hyttiälä field site in recent years, spurred in part by the development of new instruments capable of detecting ever smaller particles and chemically identifying their gas phase precursors (Kulmala et al., 2013; Schobesberger et al., 2013). Sulfuric acid is thought to be an important NPF precursor here and in general (e.g., Kuang et al., 2010; Zhang et al., 2012). Sulfuric acid concentrations at Hyttiälä are higher during NPF event days, and increased ultrafine particle sulfate fractions were observed to increase at the start of an event (Bzdek et al., 2012; Kulmala et al., 2013; Smith et al., 2010). Organics correlated with Hyttiälä NPF events include short-chain (<C11) alkanolic acids detected in the aerosol phase (Anttila et al., 2005), and organic highly oxygenated molecules generated from the ozonolysis and rapid autoxidation of biogenic terpenoids and detected in the gas phase (Ehn et al., 2014; Rissanen et al., 2014). Mäkelä, Yli-Koivisto, and Hiltunen (2001) also found enhancement of methanesulfonic acid (MSA) in the nucleation mode during NPF events, and much higher levels of dimethylamine (DMA) in ultrafine

aerosol overall. Smith et al. (2010) found methylammonium to be the main aminium salt component in recently formed ultrafine particles. Overall, these observations imply that the condensation of low volatility highly oxygenated organics and sulfuric acid and the formation of organic and inorganic salts drive growth of newly formed particles at this site.

The correlation of the dimethylsulfide (DMS) oxidation product MSA with NPF suggests a role for marine air in this process. NPF events are more common in air with northwesterly trajectories, associated with transport over the relatively unpopulated northern Nordic region from the North Atlantic and Arctic Oceans (Dal Maso et al., 2005; Mäkelä et al., 2000; Nilsson & Kulmala, 2006). The apparent marine effect may be due to a lower aerosol condensation sink for nucleating vapors compared with continental air masses, allowing a larger fraction of the available low volatility compounds to contribute to NPF. In addition, it is also possible that the marine atmosphere provides important chemical precursors. DMS may be one such precursor, leading to the formation of sulfuric acid as well as MSA, which can also undergo NPF reactions (Chen et al., 2016).

In highly controlled laboratory experiments at CLOUD in CERN, the observation of stepwise molecular additions of well-identified precursor species to growing molecular clusters has informed our view of atmospheric nucleation, both for systems of sulfuric acid with gas phase bases and for oxidized organic molecules produced from common biogenic precursors (Almeida et al., 2013; Kirkby et al., 2011; Schobesberger et al., 2013; Tröstl et al., 2016). However, molecular cluster measurements under ambient conditions are harder to interpret, making it difficult to infer NPF chemistry in the atmosphere (Schobesberger et al., 2013).

We present observations of the chemical composition of recently formed ambient aerosol in the size range of about 20–70 nm made at Hyytiälä in the Finnish boreal forest. These observations have sufficient time resolution to identify changes over the course of individual NPF events and sufficient chemical specificity to identify some of the key species involved. We use this unique data set to highlight some of the processes involved in NPF in this environment.

## 2. Materials and Methods

### 2.1. Field Site Conditions

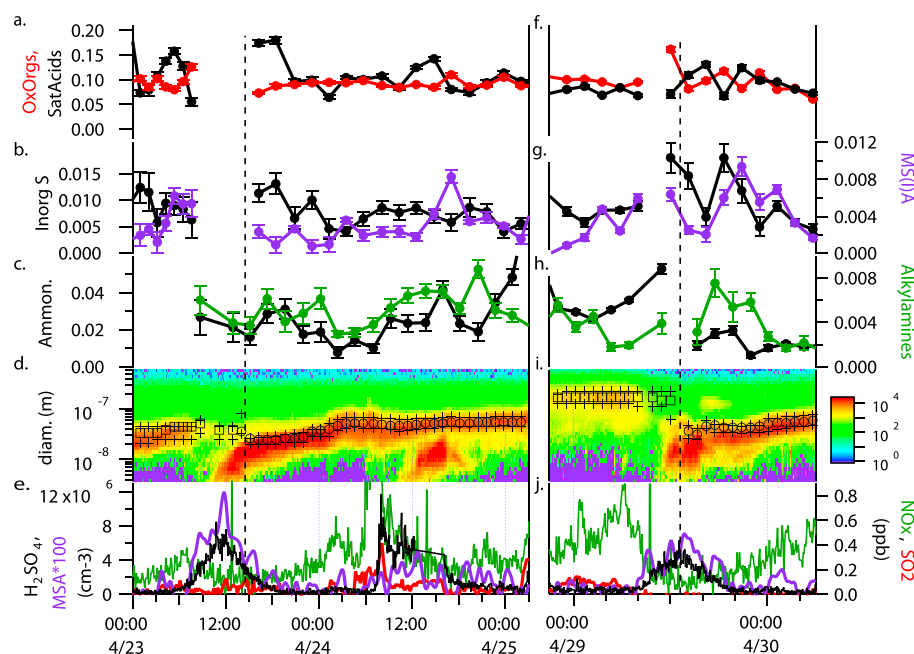
The well-characterized Hyytiälä field station is located in a stand of Scots pine (*Pinus sylvestris*) at a lake in southwestern Finland (61.8475°N, 24.2950°E) (Hari & Kulmala, 2005; Kulmala et al., 2000). The nanoparticle observations reported here were made over a period from 23 April to 1 May 2014, during the Biogenic Aerosols-Effects on Clouds and Climate (BAECC) field campaign (Petäjä et al., 2016). During this period the wind was predominantly from the northwest. Temperatures ranged from a nighttime minimum of  $-4^{\circ}\text{C}$  to a  $17^{\circ}\text{C}$  maximum in the afternoon. Conditions were mostly sunny from 22 to 26 April, with increasing cloudiness afterward, leading to rain on 28 April. Wind speeds ranged from  $0.5$  to  $6.9\text{ m s}^{-1}$  (10 min averaged).

### 2.2. Instrument: Time-of-Flight Thermal Desorption Chemical Ionization Mass Spectrometer

The Thermal Desorption Chemical Ionization Mass Spectrometer (TDCIMS) has been described in detail elsewhere (Lawler et al., 2014; Smith & Rathbone, 2008; Voisin et al., 2003). Briefly, it can identify the organic and inorganic components present in recently formed ultrafine particles as small as  $\sim 10\text{ nm}$  by ionizing and size-selecting the particles, electrostatically precipitating them on a Pt filament, thermally volatilizing their constituents, and detecting the resultant gas phase molecules by chemical ionization via  $(\text{H}_2\text{O})_n\text{H}_3\text{O}^+$  or  $(\text{H}_2\text{O})_n\text{O}_2^-$  reagent ions. A regular cycle during these observations included 30 min of collection, then 30 min of background assessment of gas phase interferences, for each ion polarity, for a total cycle of roughly 2 hr. Backgrounds were assessed by turning off the filament high voltage. The collected particle sizes were assessed using a scanning mobility particle sizer (TSI 3085 and TSI 3025) downstream of the TDCIMS collection wire by comparing collection and background period. A separate condensation particle counter (TSI 3025) also monitored the sample flow downstream of the TDCIMS collection wire to measure the total sampled particle number.

### 2.3. Supporting Observations

The Hyytiälä site supports several continuous observations which are available on the SMEAR website (<http://avaa.tdata.fi/web/smart>) (Junninen et al., 2009). From this database we used gas phase nitrogen oxides ( $\text{NO}_x$ :  $\text{NO}_2 + \text{NO}$ ) and sulfur dioxide ( $\text{SO}_2$ ), as well as wind speed and direction, and the particle size distribution as



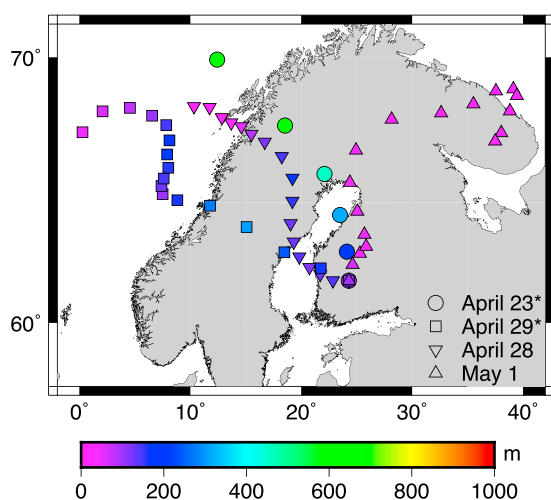
**Figure 1.** Particle and gas phase observations around the events of 23 and 29 April. Particle measurements before the vertical dashed lines are primarily of pre-event aerosol. Particle phase negative ion fractions for (a and f) oxidized hydrocarbons with greater than five oxygen atoms (OxOrgs) and the sum of alkanolic acids and linear, unsubstituted saturated dicarboxylic acids (SatAcids) and ion fractions for (b and g) methanesulfonate and methanesulfinate (MS(I)A) and sulfur salts (Inorg S). Negative ion data for <70 pg collected mass were excluded due to low signal-to-noise. Positive mode ion fractions of (c and h) ammonium (Ammon.) and alkylammonium (Alkylamines). (d and i) Ambient aerosol size distribution ( $dN/d\log D_p$ ) and particle diameters collected for thermal desorption chemical ionization mass spectrometer (TDCIMS) analysis. The circles are volume median diameter (VMD) of collected particles assessed by direct measurements. The squares are VMD as assessed by analysis of ambient size distributions and number concentration measured after the TDCIMS wire. The crosses represent the range of particle sizes composing 90% of the total collected mass. (e and j) Gas phase observations of sulfuric acid ( $\text{H}_2\text{SO}_4$ ), methanesulfonic acid (MSA),  $\text{NO}_x$  ( $\text{NO}_2 + \text{NO}$ ), and sulfur dioxide ( $\text{SO}_2$ ).

measured by a differential mobility particle sizer (Aalto et al., 2001). In addition, gas phase sulfuric acid ( $\text{H}_2\text{SO}_4$ ) and MSA were measured by nitrate addition chemical ionization mass spectrometry using an atmospheric pressure interface time-of-flight mass spectrometer (Aerodyne Research, Inc.) after the design of Eisele and Tanner (1993) and detailed in Jokinen et al. (2012).

### 3. Observational Results

### 3.1. Events and Air Mass Origins

Two intense NPF events lasting more than 12 hr were observed while the TDCIMS was fully operational, one on 23 April and one on 29 April 2014 (Figure 1d). Increased sub-10 nm particle number concentrations were apparent by late morning in both cases, typical of springtime NPF events at Hyytiälä (Dal Maso et al., 2005). The 23 April event was preceded by an event on 22 April, while prior to the 29 April event, the background particles were much larger and older. On April 23 the winds were northerly and reached about  $5 \text{ m s}^{-1}$  around midday. The highest wind speeds of the campaign occurred on 29 April, about  $6 \text{ m s}^{-1}$  around midday (Figure S1f). The 23 April event was followed by a continuation of its growth mode during most of the subsequent 3 days and possibly longer (Figures 1d and S1d). This implies that it was a very widespread regional event and also that the airflow conditions were less dynamic after the event. This is confirmed by a back trajectory analysis (next paragraph). A brief, intense NPF event occurred on the following day (24 April), concomitant with growth of the mode that began on 23 April (Figure 1d). This new nucleation mode decreased in number abruptly around 17:00 local time (UTC +2) on 24 April, as the air mass histories transitioned away from rapid marine transport. Every day there was some particle number enhancement at sub-20 nm sizes (Figure S1d), but only days with a relatively low condensation sink (below about  $1\text{--}2 \times 10^{-3} \text{ s}^{-1}$  for  $\text{H}_2\text{SO}_4$ )



**Figure 2.** Air mass back trajectories arriving at the site in 2014 at 100 m elevation at 12:00 local time on the days of two events, 23 April (circle) and 29 April (squares), and on two nonevent days, 28 April (downward triangles) and 1 May (upward triangles), calculated using the Hybrid Single Particle Lagrangian Integrated Trajectory Model. The time between points for each trajectory is 6 hr. Complete 4 day back trajectories are shown with the exception of the 23rd, which showed transport in the lower atmosphere from northern Greenland and was cropped for clarity. The two strong event days are indicated by an asterisk in the legend.

showed NPF events with growth beyond about 30 nm (23 and 29 April). The condensation sink was calculated after Dal Maso et al. (2002) for an  $\text{H}_2\text{SO}_4$  diffusion coefficient of  $0.075 \text{ cm}^2 \text{ s}^{-1}$  (Brus et al., 2016). Ultrafine particle number enhancement was strongly correlated with wind speed (Figure S8). The 29 April event lasted only about 21 hr, a more typical timescale for the Hyytiälä events than the lengthy 23 April event.

Four-day air mass back trajectories for air arriving at the site were calculated using the Hybrid Single Particle Lagrangian Integrated Trajectory Model online model with Reanalysis data (<http://ready.arl.noaa.gov/HYSPLIT.php>) (Rolph et al., 2017; Stein et al., 2015). Trajectories were computed for air arriving at the site at 00:00, 06:00, 12:00, and 18:00 local time each day. For the events of 23 and 29 April, as well as the brief 24 April event, the 12:00 back trajectories showed that the air masses had been over the Atlantic Ocean within 1–2 days, as a result of the relatively high wind speeds (Figures 2 and S1f). For the days without strong events (25–28 April), the air masses spent more time circulating over the Scandinavian landmass and the Bay of Bothnia. The longevity of an individual NPF event appears to depend on the time the air mass spent over the continent. It seems likely that NPF occurs simultaneously over much of Fennoscandia and that the growth mode from the events is observable at Hyytiälä as long as the air measured at the site had been over the continent after the onset of the regional NPF event. During the week of sampling, particles from apparent regional NPF events were observed when the sampled air had been over the ocean within the previous 4 days. After midday on 30 April, the air mass origins shifted to the east, away from the ocean, and a clear NPF event was not observed until 3 May, when the air mass back trajectories shifted to the North Atlantic. Of eight clear NPF events ( $>2,000 \text{ cm}^3$  sub-20 nm particles) during the intensive period of 14 April to 3 May 2014, all included air masses that had been over the ocean within 1.5 days and half of them within 24 hr.

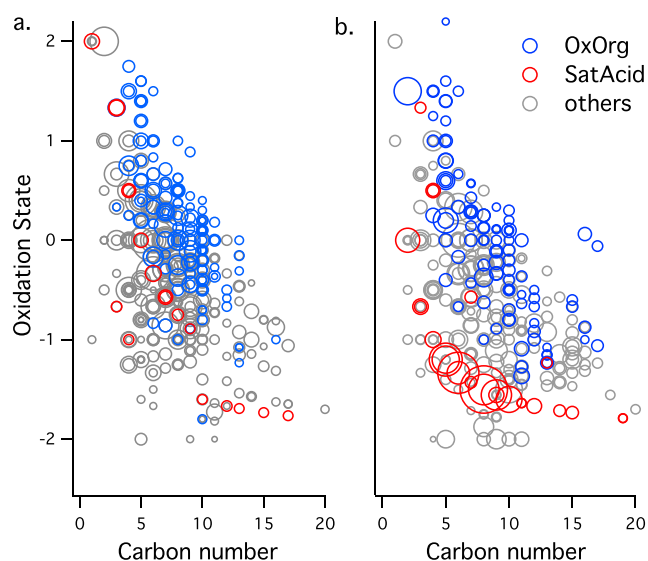
### 3.2. TDCIMS Collected Particles

Ambient particle collections with well-resolved volume median diameters as small as 25 nm were achieved during the NPF events (Figures 1d and 1i and supporting information S1). By increasing the nano-DMA set points up to 30 nm, it was possible to collect well-defined, size-resolved nanoparticles up to a volume median diameter of 58 nm (McMurry et al., 2009). At a nominal set point of 40 nm, the collected particle mass was dominated by particles larger than the  $\sim 80$  nm size limit of the scanning mobility particle sizer system (Figure S2). Collected masses for well-defined particle collections ranged from 0.03 to 0.82 ng, assuming a  $1 \text{ g cm}^{-3}$  density for simplicity. The TDCIMS sum detectable ion signal showed a strong linear correlation with the total mass collected for these well-defined mass collections ( $r^2 = 0.82$  for neg ions,  $r^2 = 0.84$  for pos ions). By extrapolation, collected masses at a nominal set point of 40 nm ranged from 0.13 to 2.4 ng.

### 3.3. TDCIMS Composition Observations

The TDCIMS composition results are presented as ion fractions of major classes of compound detected (Figures 1a–1h). In both positive and negative ion modes, organics essentially always made up over 90% of the total signal. Ions consistent with linear carboxylic and dicarboxylic acids with 0–2 double bonds typically represented about 25% (and as much as 35%) of the negative ion signal.  $\text{C}_2\text{--C}_{11}$  species of this type were detected, with  $\text{C}_6$  and  $\text{C}_8$  alkanolic acids and a mono-unsaturated  $\text{C}_6$  diacid showing large contributions (Figure S3). About half of the apparent acid signal was represented by saturated linear acids (SatAcids). The SatAcids showed that the largest relative increases of any identified group when newly formed particles were sampled, reaching up to 18% of the negative ion signal (Figures 1a and 1f). They were also the group showing the best correlation with number of ambient 4–50 nm particles ( $r^2 = 0.28$ ,  $p = 1.2 \times 10^{-6}$ ; Figure S6.). No other identified chemical group showed a statistically significant correlation ( $p = 0.05$ ). Negative ions containing only C, H, and O atoms and having more than five O atoms





**Figure 3.** Carbon oxidation state of organic species detected by thermal desorption chemical ionization mass spectrometer in negative ion mode for (a) a chamber new particle formation experiment with collected ~30 nm particles formed from oxidation products of alpha-pinene and delta-3-carene and (b) recently formed ~25 nm particles at the Hyytiälä field site sampled from 15:42–16:12 local time on 23 April 2014. The area of the circles indicates relative signal intensity. The same high resolution ion peak list was used for both data sets. The colors indicate the ion type from Figure 1a: OxOrg (blue), SatAcids (red), and others (gray).

were grouped into a highly oxidized organics category (OxOrgs). These represent both actual molecular ions of the species present in the particle phase and fragments that result from thermal or ionization-induced decomposition of the particle phase species. These species reached their highest signal fractions (up to 16%) in preexisting aerosol at the beginning of the events (Figures 1a and 1f). The bulk of the organic ions are consistent with terpenoid oxidation products, based on their H:C ratios, carbon numbers, and their similarity with particles formed from known monoterpene precursors, but with an additional influence from the SatAcids (Figure 3).

Sulfate and sulfonate salts (S salts), identified by their decomposition to form  $\text{SO}_2^-$  and  $\text{SO}_3^-$  ions, represented only about 1% of the negative ion signal. These were higher than average during the half day following the events on 23 and 29 (and the 22), with a clear enhancement relative to background aerosol on 29. Molecular MSA and its precursor methanesulfonic acid were observed at ion fractions less than 1% and were not always enhanced in newly formed particles. However, the brief event on 24 April was clearly associated with a sharp increase in these organic sulfur acids in the Aitken mode particles sampled (Figure 1b).

While the collected particles early on 23 April were primarily from the recently formed <100 nm mode from an event begun the previous day, the collected particles early on 29 April were primarily >100 nm accumulation mode particles probably formed at least 2 days prior. These older, larger particles had a higher ammonium fraction and a lower carboxylic acid fraction than the smaller, more recently formed particles. The aminium fractions were comparable in the two particle modes.

## 4. Discussion

### 4.1. Salt Formation

The slightly higher inorganic sulfur fraction in the newly formed particles indicates that sulfate and/or sulfonate salt formation played a larger role in the early growth of particles than later on. But these salts only represented a small fraction of the total particle signal. Pennington et al. (2013) found that sulfate dominated growth of 15–21 nm particles during NPF. The present results imply that there is a shift to organics-dominated growth above this size. Gas phase MSA reached its highest levels on the event days 23 and 29 April but was about 2 orders of magnitude lower in concentration than  $\text{H}_2\text{SO}_4$  (Figure S1e).

Ammonium was often present at much greater fractions in the accumulation mode particles observed compared with the nucleation mode particles, as much as 18% of the positive ion signal (Figure S1). The alkylammonium:ammonium ratio in the observed particles was typically about 0.5 in recently formed small particles and was typically 0.1–0.25 in the larger particles (see Figure S1c). This indicates that the alkylamines had preferential uptake to form salts in the smallest observed particles, consistent with their higher basicities and greater enhancement of nucleation rates with respect to ammonia (Almeida et al., 2013; Barsanti et al., 2009; Smith et al., 2010). The aminium fractions in these measurements were lower than in the Smith et al. (2010) observations, likely due to both the ability to measure hundreds more organic ions with the more sensitive time-of-flight mass analyzer and the collection of slightly larger particles (see Riipinen et al., 2012).

There were no gas phase observations of amines during these observations. Previous measurements at this site are few and widely differing. Kieloaho et al. (2013) found small alkylamines at levels of tens of parts per trillion by volume (ppt). Sipilä et al. (2015) determined an upper limit for DMA of 0.15 ppt. The presence of as little as 5 ppt of DMA is enough to increase rates of NPF by about 6 orders of magnitude with respect to sulfuric acid and water alone (Almeida et al., 2013). Ambient gas phase ammonia levels are almost certainly higher than the DMA levels, and the presence of 5 ppt DMA may only increase nucleation rates by a factor of about 1,000 with respect to sulfuric acid-ammonia-water nucleation, possibly with nonlinear enhancements

when both ammonia and DMA are present (Almeida et al., 2013; Yu et al., 2012). We estimate an equivalent of 0.1–0.7 ppt boundary layer DMA bound in ambient sub-100 nm particles during the present study, based on lab calibrations of dimethylammonium sulfate. If gas phase mixing ratios were at comparable or higher levels, it is likely that DMA acted to enhance the rates of NPF for the observed events.

#### 4.2. Organics Contributing to Growth

It is clear from recent experiments that highly oxidized, very low volatility, particle-forming compounds can be formed from ozonolysis of unsaturated terpenoid precursors present in the boreal forest (Ehn et al., 2014; Rissanen et al., 2014; Zhao et al., 2013). Ehn et al. (2014) demonstrated that highly oxidized monoterpene ozonolysis products were present in the right gas phase concentration range to explain most of the growth of 5–50 nm particles during NPF at Hyytiälä. Vogel et al. (2016) showed relative enhancements in such very low volatility products, including sesquiterpene oxidation products, during NPF. These species are essentially nonvolatile and are likely thermally decomposed at least in part during analysis by TDCIMS. Our measurements do indicate a role for smaller organic acids, consistent with the particle phase measurements of Anttila et al. (2005). To be clear, the molecular formulae of the species detected by TDCIMS are consistent with alkanolic acids, but we cannot exclude other molecules with identical formulae or the breakdown of larger molecules during analysis. In either case, the observed series of monocarboxylic acids is unlikely to arise from reactions of mono- or sesquiterpenes, and in laboratory NPF experiments with monoterpene precursors, we have not observed them (Figure 3). Possible sources of linear chain organic acids to aerosol include leaf waxes and transport from the marine atmosphere (e.g., Beri & Lemon, 1970; Tervahattu, 2002). Kourtchev et al. (2013) reported the presence of fatty acids in total (not size-resolved) Hyytiälä aerosol only on days of clean marine air mass influence, suggesting either that these compounds are not sourced in the forest or they are destroyed under polluted conditions.

#### 4.3. Ocean-Forest Interactions

The regional events observed here appear to be restricted to the continent, and the bulk of the material contributing to ultrafine particle growth is almost certainly composed of forest biogenic compounds and/or their oxidation products, based on both direct chemical observations and on the relationship between inferred biogenic emissions and particle growth (Tunved et al., 2006). However, several observations suggest a possible role of marine-derived compounds in NPF at this site, including the appearance of likely (MSA) and possible (amines and alkanolic acids) marine-derived compounds and the observation of strong events after rapid transport of marine air.

On 23 and 24 April, smooth particle growth from undetectably small sizes was observed. Both of these days had back trajectories indicating rapid transport from the marine atmosphere. At 6 a.m. each day, the air had been over the ocean within about 1.5 days. For the 29 April NPF event, the classic “banana” growth profile was not observed, and new particles at sizes around 8 nm appeared around 11 a.m. without a clear preceding growth period. Back trajectories early on this day indicate that the sampled air mass had not recently been over the ocean (Figure S7). By noon, when the newly formed particles were apparent, the sampled air had been in the marine boundary layer within only about a day. While previous statistical studies have indicated that clean marine and Arctic air masses result in higher NPF probabilities (Sogacheva et al., 2005, 2008), a possible enhancement of NPF likelihood due to rapid marine air transport has not been fully explored.

Marine air may provide important chemical species, such as organic sulfur compounds like DMS. DMS is oxidized to form methanesulfinic acid, MSA, sulfur dioxide, and sulfuric acid and has a lifetime on the order of a day (e.g., Lenschow et al., 1999; von Glasow & Crutzen, 2004). Atmospheric DMS mixing ratios of hundreds of ppt are not uncommon over productive North Atlantic waters (e.g., Marandino et al., 2008; Bell et al., 2013). Therefore, it is likely that at least tens of ppt of DMS may sometimes reach the Hyytiälä site given relatively rapid transport from the ocean, potentially representing a significant source of gas phase precursors for NPF. Similarly, transported marine carboxylic acids may be more likely to persist with rapid transport. The apparent daily photochemical production of MSA at the site indicates that some DMS is regularly present. The highest gas phase MSA mixing ratios were measured on the two event days, reaching  $1 \times 10^5 \text{ cm}^{-3}$ . These maxima likely result from a combination of rapid transport of marine air and very low condensation sinks. At these low levels, MSA did not likely compete with sulfuric acid in the nucleation or growth of new

particles during this study. However, DMS oxidation upwind of the site may represent a significant source of SO<sub>2</sub>, leading to sulfuric acid and NPF. At levels of 50–100 ppt DMS over the ocean, about 10–30 ppt of SO<sub>2</sub> can be produced daily (von Glasow & Crutzen, 2004), which would represent a substantial fraction of the SO<sub>2</sub> at Hyttiälä under clean conditions. We have argued that amines and alkanolic acids appear to be involved in NPF at this site, and these are both known to have marine as well as land sources (e.g., Beri & Lemon, 1970; Decesari et al., 2011; Facchini et al., 2008; You et al., 2014).

The annual cycle of NPF events is also suggestive of a marine influence, as it roughly matches the seasonal cycle of marine phytoplankton concentration near the Nordic coast, with spring and fall local maxima (Colebrook, 1979; Dal Maso et al., 2005). Furthermore, April is the month when DMS concentrations typically begin to increase in the Atlantic Subarctic region, as a result of the spring phytoplankton bloom (Lana et al., 2011). If the ocean provides NPF-relevant biogenic organic compounds, it seems likely that the greatest flux would be during bloom periods.

Recent global-scale modeling studies which include microphysical aerosol processes have indicated that marine DMS emissions do not exert a strong control on CCN and that changes in emission strength would have little impact on climate (Woodhouse et al., 2010, 2013). Woodhouse et al. (2013) estimate only a 1–2% increase in annually averaged CCN in the southern Finnish boreal forest when DMS emissions are included in the model. Their explanation for the small effect is that SO<sub>2</sub> produced from DMS oxidation is only inefficiently converted to H<sub>2</sub>SO<sub>4</sub>. This may be the case in many regions. However, NPF occurs frequently at Hyttiälä; it has been tied to H<sub>2</sub>SO<sub>4</sub> formed in situ from SO<sub>2</sub> oxidation, and the newly formed particles have been demonstrated to result in CCN (Kerminen et al., 2005). We have presented inferential evidence that DMS may be a source of SO<sub>2</sub> and H<sub>2</sub>SO<sub>4</sub> at Hyttiälä. If this is the case, it seems likely that DMS has an impact on CCN in at least some Nordic regions. High-quality in situ measurements of DMS and SO<sub>2</sub> of sufficient length and precision to capture seasonal patterns and diel cycles are necessary to answer this question, and to isolate the influence of marine air from that of continental pollution.

## 5. Conclusions

We sampled and chemically analyzed recently formed, size-resolved ambient nanoparticles in the southwest Finnish boreal forest using TDCIMS. These observations indicate a possible enhancement of highly oxidized hydrocarbons and sulfur salts at the beginning of events and showed that most growth to 20–70 nm sizes can likely be attributed to terpene oxidation products. However, newly formed particles in this size range were associated with higher fractions of non-terpene-derived saturated organics consistent with alkanolic acids. Alkylamines are likely important drivers of NPF in this environment, though their gas phase mixing ratios are uncertain. Some evidence points to a possible role for ocean-derived species in NPF events in the forest. We advocate further efforts to determine whether ocean emissions impact downwind boreal forest NPF, both through targeted precursor observations and further statistical analyses that consider marine air transport to the forest.

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